



Short communication

Qualitative lead extraction from recycled lead–acid batteries slag

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ABSTRACT

The pyrometallurgical process that the exhausted batteries are submitted for the recovery of metallic lead generates great amount of a by-product called slag. The slag is composed mainly of iron ($\approx 60\%$) and lead ($\approx 6\%$), and this residue cannot be disposed in conventional landfill due to the high lead content. This work presents a new methodology for the extraction of lead from slag, based on the complexing effect of EDTA, a chelating ligand that has the ability to solubilize several heavy metals. As the iron ($\text{Fe}^{2+}/\text{Fe}^{3+}$) have a formation's constant with EDTA higher than the lead and is present in high concentrations in the samples, the fluoride ion (F^-) was employed to mask the iron ions. The tests were carried out in a qualitative way, confirming the lead extraction by the formation of a yellow precipitate of lead iodide.

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1. Introduction

The lead–acid batteries represent about 60% of batteries sold in the entire world [1–3]. Lead is a material very easy to recycle and, provided that adequate procedures are implemented, the final product (secondary lead) is indistinguishable from the primary lead produced from ores. About 50% of the lead consumed worldwide is derived from recycled and reused materials [4].

The recovery of metals from metal scrap has the advantage that it is easier and far less energy dependent than the production of primary lead from ores. The production of recycled lead requires 35–40% of the energy necessary to produce lead from ores. In addition, the recovery of lead decreases the lead dispersion in the environment and preserves the mineral reserves for the future. It is estimated that at least 85% of the consumed lead can potentially be recycled [4,5].

According to Jolly and Rhin, about 47% of total lead production comes from secondary smelting, and 85% of the lead–acid batteries are recycled. Two constituents of batteries can be recycled: the lead and polypropylene. Effective release processes and subsequent separation are required to enhance the two products and stabilize the others (sulfuric acids and separation envelopes) [5].

The batteries are broken, crushed and automatically separated into various components: carcass materials, metal poles and grids, and lead oxide/sulfate pastes. The acid is collected and completely neutralized before its disposal or reuse by other industries. The plastic material (about 5% weight in battery) is separated in polypropylene and other plastics (rubber, PE, etc.). The metallic components (55% weight in battery) are classified for the smelting. The pastes, consisting of a mixture of lead oxides and sulfates, are usually treated to remove most of the sulfur [4,5].

At the smelting step, named pyrometallurgical process, the lead compounds from the break are reduced to provide metallic lead with low antimony content, by smelting the battery paste (lead oxide/hydroxide/carbonate, with a small amount of sulfate) with coke or other reducing agent rich in carbon and sodium hydroxide (NaOH) and sodium nitrate (NaNO_3) for the removal of other metals (Cu, Sn, As, Ag, etc.) in the oxide form. The reduction of waste sulfates derived from the battery electrolyte leads to sulfides (NaFeS_2 , FeS , FeS_2 , Na_2S). The equipment used is a rotary furnace, short or long, to minimize the amount of waste [4,6].

The main lead reserves are located in United States of America, Australia, Canada, Peru and Mexico being these countries the highest producers of this metal. About 60% of the metallic lead produced in the world comes from minerals, and around 3 millions of tons are produced every year [4].

According to Lassini et al., the lead recycle represents the most correct procedure in the environmental point of view, but that does not mean that the recycling process might not cause problems to the environment and human health. The lead recycling industry is

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potentially polluting, due to the gases and particulate emission, and to the slag that results from the recycling process. Every year the lead recycling process produces 200,000 tons of slag, in addition to 280,000 tons of the residue from the sulfuric acid neutralization (gypsite) [6].

The particle size distribution of the slag is very heterogeneous, ranging from blocks of meters in size until thin ashes. The blocks consist mainly of elongated crystals of sulfides, and the melt part at the bottom of the reactor presents a superficial film of metallic lead. There is a great variability in the chemical composition of slag, which depends very much on the efficiency of the pyrometallurgical process employed. The major phases correspond to alkaline iron sulfide (NaFeS_2) and its hydrated equivalent ($\text{NaFeS}_2 \cdot 2\text{H}_2\text{O}$), sodium carbonate, coke and lead in the metallic or sulfide form [6,7].

According to Coya et al., the slag is stored temporarily in open air deposits, where it loses its soluble components and becomes stable. For the slag to be classified as environmentally safe, a minimum aging period (about 6 months) is necessary for the slag to lixiviate under natural conditions or by washing processes, in order to lose its soluble components [7].

Nevertheless, the slag is classified like a hazardous industrial waste that can, depending on the exposure conditions, exhibit heating properties, toxicity, corrosivity, acid production (making it able for leaching), and evident environmental hazard. Being a special industrial residue, it should be treated as such.

Thus, the slag cannot be discarded in landfills or in a closed ambient (risk of gases emanation in case of oxidation). This residue cannot be disposed after forced oxidation (secondary salts solubilization) but can be stabilized due to the extension of the soluble fraction of the residue ($\approx 70\%$). It is then evident the need for studies that could find alternatives based on the utilization of this residue like a secondary material, at the same time reducing its pollutant potential.

De Angelis et al. conducted a study of waste reuse (gypsite and slag), through its immobilization in Portland cement matrix [8]. Penpolcharoen carried out an initial investigation of the reuse of powder slag in concrete blocks, replacing part of the Type I Portland cement, to evaluate its pozzolanic activity [9]. In another work, Bigelli proposed the aggregation of the slag in red pottery mass [10]. However, these applications can cause considerable changes in the properties of these materials, and, depending on the conditions of their preparation, the lead can be lixiviated from the matrix.

The removal of lead from the slag would allow a new destination for this type of waste, reducing the burden of the responsible company and, mainly, preventing possible environmental contaminations. Data in the literature about the issue of lead removal and recovery of solid wastes, most precisely, battery secondary smelting slag, are practically nonexistent.

In this way, the present work aimed to develop a method for the lead removal from the slag resulting of the automotive batteries recycling process. A method for the extraction, identification and recovery of the lead from the slag was elaborated, based on the complexing effect of EDTA.

2. Experimental

2.1. Materials

The battery slag was provided as a massive block by an automotive batteries recycling industry. The sample was broken and macerated to a particle size lower than $600\ \mu\text{m}$.

The slag presents as major compounds iron and lead in a content of about 60% and 6%, respectively. Minor metals elements com-

prehends mainly Cu, Sn and Sb in a total content lower than 0.5%, according to the data provided by the recycling industry.

The fluoride (F^-) saturated solution ($42\ \text{g L}^{-1}$) was prepared using NaF (Merck) with the aiming of masking the iron ions. In order to improve the NaF solubilization in water, the solution was heated, and the insoluble matter was removed by filtration. The fluoride concentration in the resultant solution ($18\ \text{g L}^{-1}$) was determined by Ion Exchange Chromatography (Metrohm Model 861) with chemical suppression (H_2SO_4 : $0.01\ \text{mol L}^{-1}$) with conductivity detector.

The EDTA solutions were prepared from the disodium ethylenediaminetetraacetic acid (Merck) that presents solubility in water of $100\ \text{g L}^{-1}$.

The saturated solutions of ferric (Fe^{3+}) and iodide (I^-) ions were prepared from the addition of the ferric chloride (FeCl_3) (Merck) and potassium iodide (KI) (Merck) salts, respectively, in an adequate volume of distilled water, upon stirring, until the saturation of the solution, denoted by the formation of a precipitate, which was later separated by filtration. The $3\ \text{mol L}^{-1}$ of H_2SO_4 solution was prepared from the dilution of concentrated sulfuric acid (98%, $d = 1.8\ \text{g mL}^{-1}$, Merck).

2.2. Preliminary complexation tests using Pb^{2+} salts

The objective of these preliminary tests was the development of a qualitative methodology for the confirmation of lead complexation with EDTA, to be used later when employing the real sample (slag). The method was based on the following steps: (i) complexation of the lead salts with EDTA, (ii) displacement of lead from the complex by addition of a metal with higher formation constant with EDTA and (iii) formation of a lead compound easily identifiable qualitatively (PbI_2 , yellow) by the addition of an appropriate anion (I^-).

Considering that the residual lead present in the slag is mostly in the saline form [7], the feasibility of employing the EDTA as the extractor solution of slag lead, by its solubilization, was previously evaluated employing lead salts (PbI_2 and PbSO_4) with low water solubility ($K_{\text{ps}} = 7.1 \times 10^{-9}$ and $K_{\text{ps}} = 1.6 \times 10^{-8}$, respectively) [10]. The salts (PbI_2 and PbSO_4) were generated *in situ* from saturated aqueous lead solutions ($\text{Pb}(\text{NO}_3)_2$), iodide (KI) and sulfate (H_2SO_4).

Iodide ions and different cations ($\text{M}^{n+} = \text{Ca}^{2+}$, Ba^{2+} , Mg^{2+} , Mn^{2+} , Co^{2+} , Ag^+ , Hg^{2+} , Al^{3+} , Fe^{3+} , Ni^{2+} , Cu^{2+} , Cr^{3+} , Bi^{3+}) were then added to the resulting solution, in independent runs, with the objective of displacing the lead from its complex with EDTA by the formation of a more stable complex (EDTA-M^{n+}). The displaced lead was re-precipitated in the form of PbI_2 , an easily identified salt, in a qualitative way, by its intense yellow color.

2.3. Qualitative tests of lead extraction from the slag

The qualitative tests of lead extraction of the slag were performed according to the results obtained in the preliminary tests, in which the presence of lead in solution was confirmed by the formation of a yellow precipitate of PbI_2 .

These assays were carried out by adding two (2.0) g of previously crushed slag in a beaker to 25 mL of $0.1\ \text{mol L}^{-1}$ EDTA solution. After 30 min of contact at room temperature, under mechanic stirring, the solid was separated of the solution by filtration. The resulting solution was pre-concentrated to 5.0 mL by evaporation. After cooling, it was transferred to a test tube, adding in sequence 3.0 mL of KI and 3.0 mL of Fe^{3+} saturated solutions.

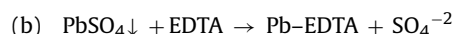
Extraction tests were also carried out, using the fluoride ion (F^-) as a complexing agent for the Fe^{3+} ions present in the slag. Therefore, two (2.0) g of crushed slag were added to a beaker with 10.0 mL of saturated solution of fluoride ions. After 10 min of contact at room temperature, under mechanic stirring, 25 mL of $0.1\ \text{mol L}^{-1}$ EDTA

solution was added to the mixture. After 30 min of reaction, the solid was separated from the solution by simple filtration and the filtrate was evaporated to 5 mL. After cooling, saturated solutions of iodide and Fe^{3+} ions (3 mL each) were added in sequence.

3. Results and discussion

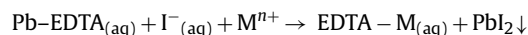
3.1. Preliminary complexation tests using Pb^{2+} salts

Both lead salts used in these assays (PbI_2 or PbSO_4) presented high solubility in the EDTA saturated solution, by the formation of the Pb–EDTA complex:



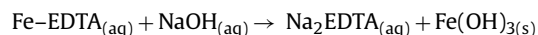
However, unlike other M^{n+} –EDTA complexes, such as the complex with chromium, which has a purple color, the Pb–EDTA complex is colorless, preventing the direct visualization of its formation, which would characterize the lead extraction from the slag [12]. Thus, a way of identification of the Pb–EDTA complex formation is needed, when real samples as the slag are treated.

For this reason, different cations were added to the resulting solutions of the solubilization step with EDTA. Iodide ions were also added to these solutions, but only in the assays using PbSO_4 as initial salt, since in the experiments with PbI_2 the iodide was already present. The addition of cations with EDTA complex formation constants higher than or near to the EDTA–Pb complex aims the displacement of lead from its EDTA complex, allowing its re-precipitation in the form of PbI_2 [13]. This latter is a yellow salt of easy visual identification. From the cations evaluated, the only that caused the displacement of the lead from its complex with EDTA were Co^{2+} , Al^{3+} , Fe^{3+} , Ni^{2+} , Cu^{2+} and Cr^{3+} .



where $\text{M}^{n+} = \text{Fe}^{3+}$, Al^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} and Cr^{3+} .

Thus, Fe^{3+} ions was chosen, due to its higher EDTA complex formation constant, this turns easy the displacement of lead from the complex, and does not interfere in the qualitative analysis by precipitation with iodide ions, like in the case of Cu^{2+} , which forms a grey precipitate of CuI_2 . Furthermore, the use of the Fe^{3+} allows the recovery of iron and EDTA, present in solution in the form of the Fe–EDTA complex (generated during the displacement step). The Fe^{3+} could be recovered by the elevation of pH (pH 12), enabling the reuse of EDTA in the dissodic form (Na_2EDTA):



3.2. Qualitative tests of lead extraction from the slag

The first assays aimed to the direct extraction of lead from the slag using EDTA as extracting agent. However, after the addition of I^- and Fe^{3+} ions, the formation of the PbI_2 yellow precipitate could not be observed. This is an indication of the absence of lead in the solution. The EDTA, used in this way, is unable to extract the lead present in the slag, despite the relatively high amounts of lead in the sample ($\approx 6.0\%$). This behavior can be due to the nonspecific complexing action of EDTA, which can react with other metals present in the reaction medium [1].

As mentioned before, the slag presents a high concentration of iron ($\text{Fe}^{2+} \ll \text{Fe}^{3+}$). Besides the high concentration of Fe^{3+} in the slag sample ($\sim 60\%$), the more stable EDTA complex ($K_{\text{Fe-EDTA}} = 1.3 \times 10^{25}$) than the Pb–EDTA ($K_{\text{Pb-EDTA}} = 1.09 \times 10^{18}$), gives it priority in relation to the lead in the dispute by the complexing agent [11–13]. This property was demonstrated in the

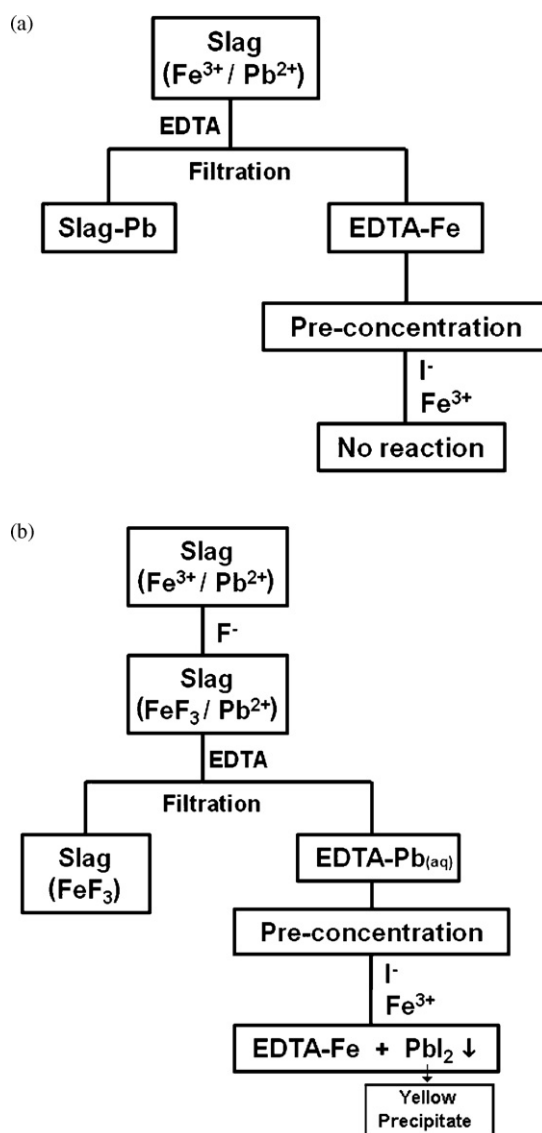


Fig. 1. Fluxogram of the procedure of extraction and identification of the Pb from the waste without the previous addition of the fluoride (a) and with the previous addition of the fluoride (b).

preliminary tests, in which the Fe^{3+} ion was one of the cations that could move effectively the lead from its complex with EDTA. In this sense, the results suggest that the presence of Fe^{3+} prevents the complexation of the lead with EDTA, and, consequently, its extraction from the sample. According to the literature, this problem can be overcome by the use of a selective complexing agent, in relation to lead, preventing Fe^{3+} from being complexed by EDTA [13].

Fig. 1 (a) shows the reaction flowchart of the lead extraction test from the slag by EDTA, without the use of a complexing agent for the Fe^{3+} present in the slag. Based on this result, lead extraction tests using fluoride (F^-) as complexing agent for Fe^{3+} from the slag and, later, the EDTA as complexing agent for the lead extraction from the slag was investigated.

For this test, the formation of the PbI_2 yellow precipitate after the addition of Fe^{3+} and I^- ions was observed, confirming the presence of lead in solution (in the form of Pb–EDTA) and, consequently, the effectiveness of the extraction step with EDTA. The fluoride ions, added previously to EDTA, act as complexing agents for the Fe^{3+} ions present in the sample, preventing its reaction with EDTA by the formation of the FeF_3 compound. When adding the EDTA solution to

the sample, the Fe^{3+} ions, masked by fluoride, no more compete with lead for the complexing agent. In this step of the process, lead is the metal present in the sample with the highest probability of being complexed by EDTA. The lead in solution, in the form of the Pb–EDTA complex, was separated from the residual solids by filtration. Later, after the addition of Fe^{3+} ions, the lead is displaced from its complex with EDTA, and in the presence of iodide ions, precipitates in the form of PbI_2 (yellow).

The reaction flowchart shown in Fig. 1(b) summarizes the main steps of the lead extraction from the slag, carried out in the presence of the masking agent (fluoride ions).

The sensitivity of the procedure, regarding to the minimum lead concentration required for the occurrence of the displacement and re-precipitation reactions, was evaluated using standard lead solutions. The formation of the PbI_2 precipitate was possible for solutions containing at least 100 mg L^{-1} of lead.

Other masking agents for Fe^{3+} , as cyanide and triethanolamine, were evaluated [13]. The best results were obtained only when fluoride ions were used as complexing agents. When cyanide was used as masking agent of iron ions, gas bubbles (HCN) were observed, probably due to the acid character of EDTA and Fe^{3+} present in the solution. The formation of the highly toxic HCN gas is reported at pH values lower than 11 [13].

4. Conclusions

The re-precipitation of the lead as PbI_2 , a solid with intense yellow color, has shown to be a feasible parameter for the qualitative identification of lead in solutions, proving the validity of the extraction procedure.

The complexity of the sample, mainly characterized by the presence of Fe^{3+} , does not allow the direct use of EDTA. As a good

contribution, we have observed that the Fe^{3+} interference was overcome by the use of fluorine as complexing agent.

The method developed in this work was efficient for lead extraction from the slag, presenting as a promising route for application in several kinds of contaminated by lead residues.

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